Derivation of the HNC Free Energy Expression

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Outline

- Some words about DFT
- HNC closure
- HNC Free Energy Expression
- 6D OZ expression vs RISM HNC expression

Free energy functional

We define free energy functional which depends on **one dimensional** density $\rho(\mathbf{r})$

However, explicit view is written for the **N-dimensional** partition function $\rho^{(N)}(\mathbf{r})$

$$F[\rho] = \frac{1}{N!}\int d\mathbf{r}^{\mathbf{N}} \rho^{(N)} \left(U(\mathbf{r}^{\mathbf{N}}) + V_{\text{ext}}(\mathbf{r}^{\mathbf{N}}) + kT \ln \Lambda^{3N} \rho^{(N)} \right)$$

Why this formula is correct?

Equilibrium partition function:

$$\rho_0^{(N)}(\mathbf{r}^N) = \frac{1}{(2\pi\hbar)^{3N}} \int \frac{1}{Z_N} e^{-\beta \sum \frac{p_i^2}{2m} - \beta U_N - \beta V_{\text{ext}}} d\mathbf{p}^N = \boxed{\frac{1}{\Lambda^{3N} Z_N} e^{-\beta (U_N + V_{\text{ext}})}}$$

Putting to the functional:

$$F[\rho] = \frac{1}{N!} \int d\mathbf{r}^{\mathbf{N}} \frac{e^{-\beta (U_N + V_{\text{ext}})}}{\Lambda^{3N} Z_N} \left(U_N + V_{\text{ext}} + kT \ln \frac{\Lambda^{3N} e^{-\beta (U_N + V_{\text{ext}})}}{\Lambda^{3N} Z_N} \right)$$

$$= \frac{1}{N!} \int d\mathbf{r}^{\mathbf{N}} \frac{e^{-\beta (U_N + V_{\text{ext}})}}{\Lambda^{3N} Z_N} \left(-kT \ln Z_N \right) = \boxed{-kT \ln Z_N}$$

Ideal gas in the external field

$$\frac{\rho^{(N)}(\mathbf{r}^N)}{N!} = \prod_{i=1}^{N} \frac{\rho(\mathbf{r}_i)}{N}$$

$$F_{ideal}[\rho] = \int d\mathbf{r}^{\mathbf{N}} \prod_{i=1}^{N} \frac{\rho(\mathbf{r}_i)}{N} \left(\sum V_{\text{ext}}(\mathbf{r}_i) + \sum kT \ln \Lambda^3 \frac{\rho(\mathbf{r}_i)}{N} + \ln \Lambda^{3N} N! \right)$$

$$= \int d\mathbf{r}_i \rho(\mathbf{r}_i) \left(V_{\text{ext}}(\mathbf{r}_i) + kT \ln \Lambda^3 \rho(\mathbf{r}_i) - kT \ln N + kT \ln N - kT \right)$$

$$\boxed{= \int \rho(\mathbf{r}) \left(V_{\text{ext}}(\mathbf{r}) + kT \left(\ln \Lambda^3 \rho(\mathbf{r}) - 1 \right) \right) d\mathbf{r}}$$

Explicit dependency on ρ(**r**)

Non-ideal case

$$F[\rho] = F_{ideal}[\rho] + F_{\text{int}}[\rho]$$

$$\text{Def:} c^{(2)}(\rho, \mathbf{r}_1, \mathbf{r}_2) = -\beta \frac{\delta^2 F_{\text{int}}[\rho]}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)}$$

$$\boxed{F[\rho] = \int \rho\left(V_{\text{ext}} + kT\left(\ln \Lambda^3 \rho - 1\right)\right) d\mathbf{r} - kT \int \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2}$$

Minimal principle

It can be proven, that the equilibrium density gives the minimal value of the free energy:

$$F[\rho_0] = \min_{\rho}\{F[\rho] : \int \rho(\mathbf{r})d\mathbf{r} = N\}$$

Using Lagrange multipliers we define

$$\Omega[\rho] \equiv F[\rho] - \mu \int \rho(\mathbf{r})d\mathbf{r}$$

And have: $$\Omega[\rho_0] = \min_{\rho}\{\Omega[\rho]\}$$

Which yields: $$\left.\frac{\delta\Omega[\rho]}{\delta\rho}\right|_{\rho_0} = 0$$

Barometric formula

$$\left.\frac{\delta\Omega[\rho]}{\delta\rho}\right|_{\rho_0} = V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}_0 \left(\frac{\delta\rho(\mathbf{r}_0)}{\delta\rho(\mathbf{r})} \ln\rho(\mathbf{r}) + \frac{\delta\rho(\mathbf{r}_0)}{\delta\rho(\mathbf{r})} - 1 \right) + \int \rho(\mathbf{r}_1) c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 - \mu = 0$$

$$V_{\text{ext}}(\mathbf{r}) + kT\ln\rho(\mathbf{r}) - kT\int \rho(\mathbf{r}_1) c^{(2)}(\mathbf{r}_1, \mathbf{r}) d\mathbf{r}_1 - \mu = 0$$

$$\boxed{\rho(\mathbf{r}) = e^{\beta\mu} \exp\left(-\beta V_{\text{ext}}(\mathbf{r}) + \int \rho(\mathbf{r}_1) c^{(2)}(\mathbf{r}_1, \mathbf{r}) d\mathbf{r}_1\right)}$$

Solute in infinite dilution

Consider two systems:

Uniform

$$\rho_0(\mathbf{r}) = \mathrm{const}$$

$$V_{\mathrm{ext}}(\mathbf{r}) = 0$$

$$c_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$$

Solute is considered as the external field

$$\rho_1(\mathbf{r}) \neq \mathrm{const}$$

$$V_{\mathrm{ext}}(\mathbf{r}) = U_{\mathrm{sol}}(\mathbf{r})$$

$$c_1^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$$

Assumption:

$$\boxed{c_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \equiv c_1^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}$$

HNC closure

$$\boxed{\rho_0 = e^{\beta\mu} \exp\left(\int \rho_0 c^{(2)}(\mathbf{r}_1, \mathbf{r}) d\mathbf{r}_1\right)} \qquad \boxed{\rho_1(\mathbf{r}) = \rho_0 + \Delta\rho(\mathbf{r})}$$

$$\boxed{\rho_0 + \Delta\rho(\mathbf{r})} = e^{\beta\mu} \exp\left(-\beta V_{\text{ext}}(\mathbf{r}) + \int \left(\rho_0 + \Delta\rho(\mathbf{r})\right) c^{(2)}(\mathbf{r}_1, \mathbf{r}) d\mathbf{r}_1\right)$$

$$= e^{\beta\mu} \exp\left(\int \rho_0 c^{(2)}(\mathbf{r}_1, \mathbf{r}) d\mathbf{r}_1\right) \exp\left(-\beta V_{\text{ext}}(\mathbf{r}) + \int \Delta\rho(\mathbf{r}) c^{(2)}(\mathbf{r}_1, \mathbf{r}) d\mathbf{r}_1\right)$$

$$\boxed{= \rho_0 \exp\left(-\beta V_{\text{ext}}(\mathbf{r}) + \int \Delta\rho(\mathbf{r}_1) c^{(2)}(\mathbf{r}_1, \mathbf{r}) d\mathbf{r}_1\right)}$$

$$\boxed{\frac{\Delta\rho}{\rho_0} = \exp\left(-\beta V_{\text{ext}}(\mathbf{r}) + \int \Delta\rho(\mathbf{r}_1) c^{(2)}(\mathbf{r}_1, \mathbf{r}) d\mathbf{r}_1\right) - 1}$$

HNC closure

$$\frac{\Delta\rho}{\rho_0} = \exp(-\beta U_{\text{sol}}(\mathbf{r}) + \int \Delta\rho(\mathbf{r}_1) c^{(2)}(\mathbf{r}_1, \mathbf{r}) d\mathbf{r}_1) - 1$$

$\Delta\rho(\mathbf{r}) \equiv \rho_0 h^U(\mathbf{r}_0, \mathbf{r})$ $\quad$ $\mathbf{r}_0$ - Position of the solute

$$\int \Delta\rho(\mathbf{r}_1) c^{(2)}(\mathbf{r}_1, \mathbf{r}) d\mathbf{r}_1 = \rho_0 \int h^U(\mathbf{r}_0, \mathbf{r}_1) c^{(2)}(\mathbf{r}_1, \mathbf{r}) d\mathbf{r}_1 \underset{\text{(From OZ)}}{=} h^U(\mathbf{r}_0, \mathbf{r}) - c^U(\mathbf{r}_0, \mathbf{r})$$

$$\boxed{h^U(\mathbf{r}) = \exp(-\beta V_{\text{ext}}(\mathbf{r}) + h^U(\mathbf{r}) - c^U(\mathbf{r})) - 1}$$

HNC free energy expression

$$U(\lambda) = U_N + \lambda V_{\text{ext}}$$

$$\boxed{\Delta F = \int_0^1 d\lambda \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle = \rho_0 \int\int g(r) V_{\text{ext}}(\mathbf{r}) d\lambda d\mathbf{r}}$$

$$h^U(\mathbf{r}) + 1 = \exp(-\beta\lambda V_{\text{ext}}(\mathbf{r}) + h^U(\mathbf{r}) - c^U(\mathbf{r}))$$

$$\frac{h^U}{d\lambda} = \underbrace{\exp(-\beta\lambda V_{\text{ext}} + h^U - c^U)}_{g = h+1} \left(-\beta V_{\text{ext}} + \frac{\partial h^U}{\partial \lambda} - \frac{\partial c^U}{\partial \lambda} \right)$$

$$\boxed{g V_{\text{ext}} = kT \left(h^U \frac{\partial h^U}{\partial \lambda} - (h^U + 1) \frac{\partial c^U}{\partial \lambda} \right)}$$

HNC free energy expression

$$gV_{\text{ext}} = kT\left(\frac{\partial}{\partial\lambda}\left(\frac{h^2}{2}\right) - h^U\frac{\partial c^U}{\partial\lambda} - \frac{\partial c^U}{\partial\lambda}\right)$$

$$\Delta F = \rho_0 \int\int g(r)V_{\text{ext}}(\mathbf{r})d\lambda d\mathbf{r} =$$

$$= \boxed{kT\rho_0\int d\mathbf{r}\left(\frac{h^2}{2} - c\right)} - kT\rho_0 \boxed{\iint h^U(\lambda)\frac{\partial c^U(\lambda)}{\partial\lambda}d\mathbf{r}d\lambda}$$

HNC free energy expression

Integration by parts:

$$\iint h^U \frac{\partial c^U}{\partial \lambda} d\mathbf{r} d\lambda = \int d\mathbf{r} h^U c^U - \iint c^U \frac{\partial h^U}{\partial \lambda} d\mathbf{r} d\lambda \qquad (1)$$

OZ equation:

$$h^U(\mathbf{r}_0, \mathbf{r}, \lambda) = c^U(\mathbf{r}_0, \mathbf{r}, \lambda) + \rho_0 \int c^U(\mathbf{r}_0, \mathbf{r}_2, \lambda) h^V(\mathbf{r}_2, \mathbf{r}) d\mathbf{r}_2$$

NB: h^V independent of λ

$$\iint h^U \frac{\partial c^U}{\partial \lambda} d\mathbf{r} d\lambda = \iint c(\mathbf{r}_0, \mathbf{r}) \frac{\partial c^U(\mathbf{r})}{\partial \lambda} d\mathbf{r} d\lambda + \rho_0 \iiint c(\mathbf{r}_0, \mathbf{r}_2) h^V(\mathbf{r}_2, \mathbf{r}) \frac{\partial c^U(\mathbf{r})}{\partial \lambda} d\mathbf{r} d\mathbf{r}_2 d\lambda$$

$$\iint c^U \frac{\partial h^U}{\partial \lambda} d\mathbf{r} d\lambda = \iint c(\mathbf{r}_0, \mathbf{r}) \frac{\partial c^U(\mathbf{r})}{\partial \lambda} d\mathbf{r} d\lambda + \rho_0 \iiint c(\mathbf{r}_0, \mathbf{r}) h^V(\mathbf{r}_2, \mathbf{r}) \frac{\partial c^U(\mathbf{r}_2)}{\partial \lambda} d\mathbf{r} d\mathbf{r}_2 d\lambda$$

Expressions are the same if we change r<->r2

Then, from (1):

$$\boxed{\iint h^U \frac{\partial c^U}{\partial \lambda} d\mathbf{r} d\lambda = \frac{1}{2} \int d\mathbf{r} h^U c^U}$$

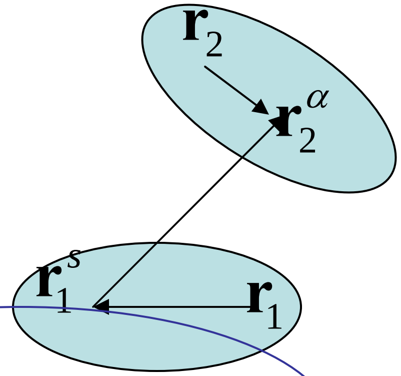
HNC free energy expression

$$\iint h^U \frac{\partial c^U}{\partial \lambda} d\mathbf{r} d\lambda = \frac{1}{2} \int d\mathbf{r} h^U c^U$$

$$\Delta F = kT\rho_0 \int d\mathbf{r} \left(\frac{h^2}{2} - c \right) - kT\rho_0 \iint h^U(\lambda) \frac{\partial c^U(\lambda)}{\partial \lambda} d\mathbf{r} d\lambda$$

$$\boxed{\Delta F = kT\rho_0 \int d\mathbf{r} \left(\frac{h^2(\mathbf{r})}{2} - c(\mathbf{r}) - \frac{h(\mathbf{r})c(\mathbf{r})}{2} \right)}$$

HNC expression in RISM



RISM assumption:

$$\boxed{c(\mathbf{r},\boldsymbol{\theta}) = \sum_{s\alpha} c_{s\alpha}(r_{s\alpha})}$$

$$\Delta F = kT\rho_0 \int \frac{h^2(\mathbf{r},\boldsymbol{\theta})}{2} d\mathbf{r}d\boldsymbol{\theta} - kT\rho_0 \sum_{s\alpha}\int c_{s\alpha} d\mathbf{r}d\boldsymbol{\theta} - \frac{1}{2}kT\rho_0 \sum_{s\alpha}\int c_{s\alpha} h(\mathbf{r},\boldsymbol{\theta}) d\mathbf{r}d\boldsymbol{\theta}$$

$$\Delta F = kT\rho_0 \sum_{s\alpha}\int \left(\cancel{\frac{h_{s\alpha}^2}{2}} - c_{s\alpha} + \frac{h_{s\alpha}c_{s\alpha}}{2} \right) d\mathbf{r}$$